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# Visualized Effects of Oxidation and Temperature on Vortex-State $Fe_3O_4$ Particles Examined by Environmental TEM and Off-Axis Electron Holography

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## Introduction

Magnetic minerals in rocks record the direction and intensity of the ambient magnetic field during formation, providing, for example, varied information about the geomagnetic field and past tectonic plate motions. Magnetite ($Fe_3O_4$) is arguably the most important naturally occurring magnetic mineral on Earth due to its high abundance and strong, dominating magnetisation and is therefore crucial to the field of palaeomagnetism. Oxidation of $Fe_3O_4$ to other iron oxides, such as $\gamma$-$Fe_2O_3$, is of interest as it effects the stability of the remanent signal of the Earth's magnetic field. Signals in $Fe_3O_4$ grains are acquired in the direction of the geomagnetic field as they cool below their Curie temperature ($T_C$) of ~ 580 °C. In order to reliably interpret palaeomagnetic measurements, the effects of chemical alteration and thermal variation on remanent magnetisation must be fully understood. Most models of such processes only exist for uniformly-magnetized grains, termed single domain (SD), whereas magnetic signals from rocks are often dominated by larger grains with non-uniform domains such as vortex states, termed pseudo-SD (PSD) grains. In order to fully understand the remanent behaviour of these non-ideal palaeomagnetic recorders, it is necessary to examine the effects of oxidation and heating on their PSD magnetic domain states directly. The transmission electron microscopy (TEM) techniques of off-axis electron holography and environmental TEM (ETEM) allow for magnetic imaging of nanoscale minerals during *in situ* heating in controlled atmospheres[1]. Here, the first use of off-axis electron holography to examine local changes in remanent and saturation magnetization in vortex-state $Fe_3O_4$ grains during *in situ* heating under vacuum and oxygen atmosphere is presented.

## Methods/Materials

Synthetic $Fe_3O_4$ particles in the PSD size range (< 200 nm) were heated *in situ* in an (E)TEM to a temperature of 700 °C under vacuum or in 9 mbar of $O_2$ atmosphere. Off-axis electron holograms were acquired at 300 kV in Lorentz mode in Titan 80-300 TEMs equipped with electron biprisms and recorded using charge-coupled device cameras, with each particle magnetized in opposite directions, in order to determine the mean inner potential contribution to the phase. For the investigation of the effect of oxidation, electron holograms were acquired after magnetisation reversal had been performed, both before and after heating to 700 °C using a Protochips heating holder. Oxidation of the $Fe_3O_4$ particles was investigated using electron energy-loss spectroscopy (EELS), through close examination of the Fe $L_{2,3}$ edges[1]. In order to examine the thermoremanent behaviour of the $Fe_3O_4$ particles, after initial magnetisation reversal at room temperature holograms were acquired in magnetic-field-free conditions in 100 °C intervals during *in situ* heating from 100 to 700 °C using a DensSolutions heating holder and again upon cooling[2,3]. The mean inner potential contribution to the phase was acquired separately at each temperature and subtracted from the original phase images to allow the construction of magnetic induction maps that are representative of the true remanent state.

## Results and Discussion

Figure 1 illustrates the effect of accelerated oxidation on the magnetization of an elongated (~ 250 nm long, ~ 150 nm wide) $Fe_3O_4$ grain[1]. A bright-field (BF) TEM image (Fig. 1a) shows a native smooth-surfaced $Fe_3O_4$ grain, while complementary EELS analysis of the Fe 2p $L_{2,3}$ edge (Fig. 1b; blue spectrum) is in good agreement with that expected for $Fe_3O_4$. Examination of the EEL spectra after *in situ* heating revealed pre- and post- peaks close to the Fe 2p $L_{2,3}$ edge (Fig. 1b; red, arrowed) that are indicative of oxidation. The effect of oxidation on the magnetism of the grain was examined using off-axis electron holography, in the form of reconstructed magnetic induction maps. The $Fe_3O_4$ grain exhibited a change in magnetisation direction from before (Fig. 1c) to after (Fig. 1d) oxidation.

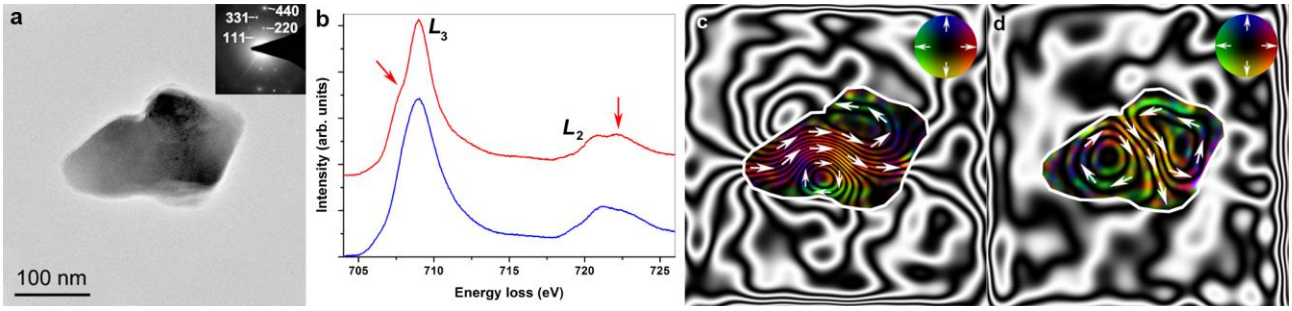


**Figure 1** (a) TEM image of an $Fe_3O_4$ particle and (b) EEL spectra acquired before (blue) and after (red) oxidation. (c, d) Magnetic induction maps of the particle (c) before and (d) after oxidation[1].

The thermomagnetic behavior of a small PSD $Fe_3O_4$ grain is presented in Fig. 2. A BF TEM image (Fig. 2a) shows the grain to be ~180 nm in length along its major axis[2]. Magnetic induction maps recorded during *in situ* heating to just below $T_C$ reveal the thermal stability of the vortex-state PSD grain. The vortex core in the small $Fe_3O_4$ grain (denoted 'v') rotates from its initial state at 20 °C (Fig. 2b) to become aligned to the major axis of the grain at 550 °C (Fig. 2c), close to its $T_C$ of ~ 580 °C. It then recovers its initial state on cooling back to 20 °C.

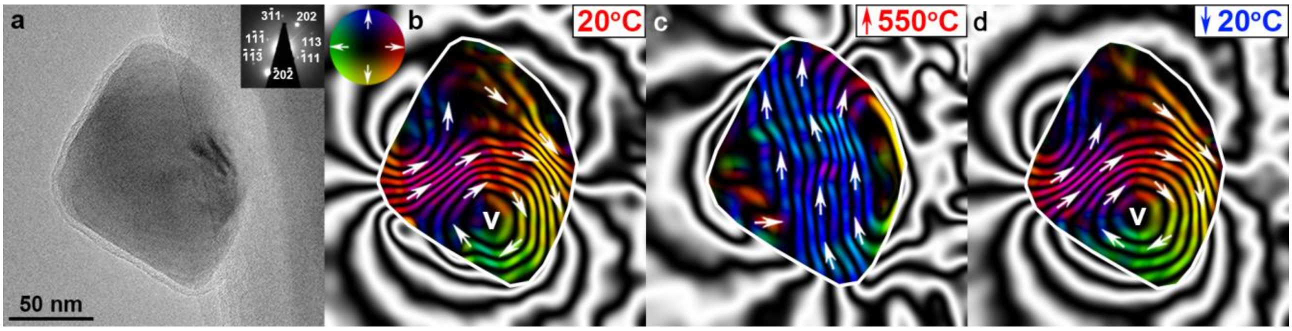


**Figure 2** (a) TEM image of an $Fe_3O_4$ particle, shown alongside magnetic induction maps recorded at (b) 20 °C; (c) during *in situ* heating to 550 °C; and (d) after cooling back to 20 °C.

Based on the present study, we infer that *in situ* heating in an $O_2$ atmosphere does indeed induce changes in both the strength and the direction of the vortex core in PSD $Fe_3O_4$ grains, confirming that oxidation can modify the original stored magnetic information. Furthermore, we show spatially resolved magnetic information from individual $Fe_3O_4$ grains as a function of temperature, which has been previously inaccessible. The $Fe_3O_4$ grain shown in Fig. 2 exhibits a dynamic movement of its magnetic vortex structure approaching $T_C$, but recovers its original state upon cooling. Hence, we demonstrate that vortex-state $Fe_3O_4$ grains, which have undergone heating events, are indeed reliable recorders of paleodirectional and paleointensity information.

## References

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